



TITLE:

Studies on the Reactivity of Vinyl Compounds. (IV) : Reactions of Vinyl Ethyl Ether and Vinyl Acetate with Carbazole

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CITATION:

Furukawa, Junji...[et al]. Studies on the Reactivity of Vinyl Compounds. (IV) : Reactions of Vinyl Ethyl Ether and Vinyl Acetate with Carbazole. 京都大学化学研究所報告 1950, 22: 84-85

ISSUE DATE:

1950-09-30

URL:

<http://hdl.handle.net/2433/74138>

RIGHT:

21. On the Properties of Polyvinylacetals Containing Sulphuric Acid.

Seizo Okamura and Takuhiko Motoyama.

The polyvinylacetals containing combined sulphuric acid were obtained by the acetalization of polyvinylalcohol using sulphuric acid as catalyst, and the combined acid in these products was also known to decrease the stability of the acetals. By the utilization of these unstabilities we could manufacture the insoluble or less-swelling films from these acetals by the baking treatment at relatively low temperature or for considerably short time.

Polyvinylacetals were prepared from polyvinylacetate (its degree of polymerization ca. 4,000) by the direct method using conc. HCl as solvent and H₂SO₄ as catalyst. The compositions of the products were as follows; degree of acetalization ca. 60%, contents of acetyl radicals ca. 3%, and sulphuric acid combined ca. 0-1.5%. All products of polyvinylacetoacetal before baking were easily soluble in methanol, ethanol, butanol or acetone. After baking at 80°C, 110°C and 130°C respectively, the products became insoluble in these solvents, and also the films obtained by the baking had the same luster as unbaked one.

Also with polyvinyl formacetal we could recognize that the swelling properties toward such a solvent as furfural, transformer-oil or dichlorethane were largely improved, but toward benzene, ethanol or water were not affected.

In conclusion, the polyvinylformal, having high degree of formalization, no acetyl groups and 0.2-0.5% combined sulphuric acid was found to be suitable for the wire insulation-coating from the standpoint of the oil-resistance.

22. Studies on the Reactivity of Vinyl Compounds. (IV)

Reactions of Vinyl Ethyl Ether and Vinyl Acetate with Carbazole.

Junji Furukawa and Mitsuhiro Goi.

a. Reaction of Vinyl Ethyl Ether with Carbazole.

Carbazole was suspended in such solvent as ether, benzene and xylene in a reaction vessel cooled with ice-water, and some drops of BF₃-etherate were added. To this mixture, with stirring, a little more than equimolecular quantity of vinyl ethyl ether diluted with solvent was added little by little. A rapid and exothermic reaction occurred. In progress of the reaction, the mixture became transparent, yellow and fluorescent. After all the carbazole was consumed, potassium carbonate was added to stop the reaction. On fractionation yellow sticky product was obtained with good yield (B.P. 178-180°C/7mm, m. p. 65-66, mol. weight (obs.) 240). On cooling and agitating it solidified to a white rhombic crystal, when cold it

had fatty feeling and when warm it became sticky. Its nitroso derivative was easily formed. The melting point above mentioned is not quite exact, for this compound did not show sharp melting point. No reaction occurred between 3-nitro carbazole and vinyl ether. Therefore, it is suggested that the reaction product might have been formed by the addition of vinyl ether to the 3rd position of carbazole. Furthermore, when this product was kept in contact with catalyst for a long time three kinds of other products were obtained, molecular weights of which were observed to be 500-600.

b. Reaction of Vinyl Acetate with carbazol.

The reaction was carried out in a similar way to that of vinyl ether. In this case mixture of BF_3 -etherate and mercuric sulfate was effective. In progress of the reaction, acetic acid splitted out. When benzene was used as solvent, an amorphous solid was obtained. Its molecular weight was observed to be about 400. And it also formed its nitroso derivative. Further details are not known about this reaction product so far.

23. The Relation between the Plastic Viscosity and Yield-point of High Polymeric Material.

Kotaro Tomihisa and Junji Furukawa.

High polymeric material behaves like an elastic body according to Hook's law (1) within a certain stress limit, the so-called yield-point (f), beyond which it flows like a pure viscous liquid showing Bingham's flow (2). Mathematically it is expressed as follows,

$$\tau = \gamma E \quad \text{for } \tau < f \quad (1)$$

$$D = \frac{d\gamma}{dt} = \frac{1}{\eta} (\tau - f) \quad \text{for } \tau > f \quad (2)$$

Where, τ is the stress: γ , E , and η are the strain, Young's modulus and plastic viscosity of the material respectively.

We used the Goodrich's plastometer for the measurement and calculated η and f of differently masticated rubbers (i.e. of different polymerities) at various temperatures by means of Scott's formula. [cf. R. Houwink: *Physikalische Eigenschaften u. Feinbau von Natur u. Kunstharz* (Leipzig 1934)].

When these values obtained are plotted on the $\ln \eta - \ln f$ diagram, they form a linear curve.

From this we conclude that f shows the same value corresponding to η , if η shows equal values, quite independent of the values of polymerity and that the higher the viscosity, the greater the yield point. As a consequence, when discussing the problem of plastic flow and liquid flow, we need only consider the flow mechanism itself.